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(54) Title: WAX COATED SILICA MATTING AGENT		
(57) Abstract <p>Wax coated silica matting agent wherein the silica is an amorphous silica having a pore size distribution wherein 90 % of the pores have a diameter above 15 nanometers, and less than 20 % of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the wax coating being present in the range from about 2 % to about 15 % by weight of the matting agent and comprising a hard microcrystalline wax, a plasticising microcrystalline wax, a synthetic polyethylene wax or a mixture thereof.</p>		

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SILICA PRODUCTS

WAX COATED SILICA MATTING AGENT

5 The invention relates to wax coated silica matting agents which are widely used in the surface coatings industry to reduce gloss but also to enhance film properties such as feel, scratch resistance and flexibility.

10 BACKGROUND TO THE INVENTION

15 It is well known that micronised waxes will impart these desirable features to the paint or lacquer film. However, when a silica is coated/impregnated with the wax a process usually performed by jointly grinding the silica and wax in a fluid energy mill (microniser), further product benefits are immediately available. The mixed phenomenon of coating and impregnating, resulting from the inherent porosity of the silica, is hereinafter referred to as "coating". The wax
20 can improve compatibility of the silica with the paint or lacquer preventing interaction with other components in the formulation. On the other hand, coating a silica with a wax can have a detrimental effect on the matting properties of the silica. In other respects, when introduced into
25 structured paints or varnishes, the coated matting agent can also destroy the thixotropy of the system.

30 It is known from EP-A-541,359 that silica matting agents coated with a mixture of a hard microcrystalline wax, a plasticizing microcrystalline wax and a synthetic polyethylene wax can prevent the formation of a non redispersible hard sediment during storage.

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Thus there is a need for a wax coated silica with matting properties at least as good as, and preferably better than, the matting properties of a naked silica.

5 Therefore it is a first goal of the present invention to provide a coated silica with matting properties which are better than the matting properties of the naked silica.

10 It is a second goal of the present invention to provide a process for manufacturing such coated silica.

It is a third goal of the present invention to provide paints and lacquers containing said coated silica.

15 It has now been found that a silica with a specific pore size distribution and a specific surface area can be coated with a specific wax in order to get matting properties previously unknown for a coated silica, when dispersed in low viscosity and low bodied thixotropic paint or varnishes
20 such as thixotropic wood lacquers.

GENERAL DESCRIPTION OF THE INVENTION

25 The present invention relates to a wax coated silica matting agent characterised in that the silica is an amorphous silica having a pore size distribution wherein 90% of the pores have a diameter above 15 nanometers, and less than 20% of the pore volume is in pores having a pore diameter
30 between 10 and 30 nanometers, the wax coating being present in the range from about 2% to about 15% by weight of the matting agent and comprising a hard microcrystalline wax, a plasticising microcrystalline wax, a synthetic polyethylene wax or a mixture thereof.

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Plasticising microcrystalline waxes have melting points in the range 70 to 85°C, a needle penetration (25°C) of from 1.5 to 3.0 mm, and is exemplified by the grades Ultraflex®, Victory® and BeSquare® 175 available from Petrolite. The hard microcrystalline waxes have melting points in the range 90 to 95°C, a needle penetration (25°C) of from 0.4 to 0.8 mm and are typified by Crown® 700 from Petrolite, Cerit® HOT from Cerilite SA, Brazil and Lunacerin® H193 from H.P.Fuller, Germany. The synthetic polyethylene wax has a melting point in the range 110 to 140°C, a molecular weight of 1000 to 4000, and is exemplified by the grades Polywax® 1000 and Polywax® 2000 available from Petrolite.

Preferably, the wax coating comprises

- i. from about 50% to about 90% by weight of a hard microcrystalline wax,
- ii. from about 5% to about 30% by weight of a plasticising microcrystalline wax, and
- iii. from about 5% to about 20% by weight of a synthetic polyethylene wax.

Such a wax coating is described in EP-A-0541359 included in the present description by reference.

Preferably, the amorphous silica has a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5% by weight in a high viscosity thixotropic system.

Preferably, the amorphous silica has a CTAB surface area of less than 100 m²/g.

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The amorphous silica is manufactured in a process in which, in a first step, sulphuric acid is added to, or mixed with, a sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of between 3.1 and 3.4 to form a slurry, after this first step the degree of neutralisation being between 50% and 88% and the SiO_2 concentration being between 6.5% and 7.5% by weight, the temperature of the slurry being maintained below 100°C and above 85°C , sulphuric acid being afterwards added to reach a pH of about 4, the resulting silica being then washed and dried.

Preferably, after the first acid addition, sodium chloride is added to reach an $\text{NaCl}:\text{SiO}_2$ ratio of 0.25:1 and 1:1. Preferably also, after the first acid addition the slurry is aged, at a temperature above 85°C , for a period of between 10 to 60 minutes.

It is therefore a second object of the present invention to provide a process for manufacturing a wax coated amorphous silica in which the components of the wax coating are blended by melting, milled to a particle size comparable with the amorphous silica, mixed with the silica in an amount of about 2% to about 15% by weight of the mixture which is then milled in a fluid energy mill to provide a wax coated silica product wherein the amorphous silica is manufactured in a process in which, in a first step, sulphuric acid is added to, or mixed with, a sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of between 3.1 and 3.4 to form a slurry, after this first step the degree of neutralisation being between 50% and 88% and the SiO_2 concentration being between 6.5% and 7.5% by weight, the temperature of the slurry being maintained below 100°C and above 85°C , sulphuric acid being afterwards added to reach a pH of about 4, the resulting silica being then washed and dried and optionally micronised.

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Definitions and Test Procedures

i. Nitrogen surface area - pore volume

Nitrogen surface area is determined by standard nitrogen adsorption methods of Brunauer, Emmett and Teller (BET) using a multi point method with an ASAP 2400 apparatus supplied by Micromeritics of the U.S.A.. The samples are outgassed under vacuum at 270°C for at least one hour before measurement. Surface area is calculated from the volume of nitrogen gas adsorbed at p/p_0 0.98. This apparatus also provides the pore size distribution from which it is possible to get the pore size (D_{10}) for which 10% of the pores are below this pore size. In the same manner, it is possible to get the pore size for which 50% (D_{50}) and 90% (D_{90}) of the pores are below this pore size. Additionally the pore volume (cm^3/g) for a given range of pore size can be obtained from the desorption curve.

ii. Matting efficiency in high viscosity thixotropic system

The matting efficiency of a silica flatting agent is determined by dispersing the silica in a polyamide-modified alkyd resin, drawing a film on a glass plate, and allowing to air dry at room temperature in a dust free atmosphere. The plates are then measured for matting efficiency at 60° and 85° incidence angle using a BYK multi glossmeter.

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Formulation of thixotropic resin

	Parts by weight
Rutile Titania	28.4
Synolac 60W (*)	22.1
Gelkyd 320W (*)	39.0
White spirit	9.3
10% Calcium carboxylate	0.7
12% Cobalt octoate	0.2
24% Zirconium carboxylate	0.2
Methyl ethyl ketoxime	0.9

(*) Synolac 60W and Gelkyd 320W can be obtained from Cray Valley Products.

This formulation, in the absence of silica matting agent, gave gloss readings of 82 and 92 at angles of incidence of 60° and 85° respectively. The viscosity of this formulation was 20,768 mPa.s at 24 sec⁻¹ and 25°C.

The test resin contains a weight percent (3% or 5%) of the silica matting agent as defined in each example.

Into an 8 oz (250 cm³) glass jar weigh 47.5 g of thixotropic resin (formulation above). Using a glass rod stir into the paint an appropriate weight of silica until the powder completely wets out. Following complete wetting stir the system at 1500 rpm for two minutes using a Heidolph stirrer (fitted with a Cowles type head). Draw a film onto a black glass plate (12" x 4") using a 100 µm block applicator and allow to air dry at room temperature, in a dust free atmosphere, over a period of 24 hours. Assess the matting

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efficiency (expressed in gloss units) by reading at 60° and 85° incidence angle using a BYK multi glossmeter.

5 iii. Matting efficiency in a low viscosity system

10 This matting efficiency was measured as under ii. but instead a thixotropic resin, a low viscosity varnish (1,600 mPa.s) was used in which the silica (coated and naked) was introduced at a loading of 6.5 % by weight based on the weight of the low viscosity varnish.

iv. Degree of neutralisation (DofN)

15 Knowing the quantity of sodium silicate which is to be neutralised it is possible to calculate the quantity of acid which is needed to complete the neutralisation. The degree of neutralisation must be understood as being the percentage of the required amount of acid
20 which has been introduced at the end of the first acid addition.

v. Weight mean particle size

25 The weight mean particle size is determined with the aid of a Malvern Mastersizer using 45 mm path length lens. This instrument, made by Malvern Instruments, Worcestershire uses the principle of Fraunhofer diffraction utilising a low power He/Ne laser. Before
30 measurement the sample was dispersed ultrasonically in water for a period of 7 minutes to form an aqueous suspension. The Malvern Mastersizer measures the weight particle size distribution of the silica. The weight mean particle size (d_{50}), the 10 percentile (d_{10}) and the

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90 percentile (d_{90}) are easily obtained from the data generated by the instrument.

vi. CTAB surface area

This method determines the specific surface area of samples, exclusive of area contained in micropores too small to admit hexadecyltrimethyl ammonium bromide (cetyltrimethyl ammonium bromide, commonly referred to as CTAB) molecules.

The isotherm for adsorption of an aqueous solution of CTAB at a charged surface has a long horizontal plateau corresponding to a bilayer coverage of the substrate surface. Rapid equilibration is achieved by using mechanical agitation. Titration with sodium dodecyl sulphate solution is used to determine the unadsorbed CTAB after removal of the dispersed silica by centrifugation.

Into a 50 cm³ screw-cap jar weigh between 0.10 and 0.25 g of silica, depending upon surface area to be determined. For high surface areas, which lead to low CTAB titrations, the lower weight is employed. Add 25 cm³ of 0.01 mol.dm⁻³ CTAB solution and bring the pH of the mixture to 9.0 with 0.1 mol.dm⁻³ NaOH solution. Stopper the jar and agitate for 1 hour in a water bath set at 25°C. Settle the suspension centrifugally and transfer 5 cm³ of the supernatant into a 50 cm³ measuring cylinder. Add 10 cm³ of deionised water, 15 cm³ of chloroform, 10 cm³ of mixed indicator solution (dimidium bromide/disulphine blue obtainable from BDH Ltd, Poole, Dorset, England) and titrate with 0.005 mol.dm⁻³ sodium dodecyl sulphate solution, previously calibrated by a standard CTAB solution. The titration

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end point is that point at which the chloroform layer becomes pale-pink. Record the volume of sodium dodecyl sulphate to reach the end point as V_2 cm³. Conduct a blank titration in a similar manner on 5 cm³ of the stock CTAB solution and record the volume of sodium dodecyl sulphate as V_1 cm³.

Calculate the CTAB surface per gram of silica by the following equation in which the calculation is based on a molecular cross section of the bromide of 35 Å²:

$$\text{CTAB surface area} = \frac{(V_1 - V_2) \times 5.27 \times (0.5)}{W}$$

Where W = Weight of silica sample (in grams)
0.5 accounts for bi-layer formation.

vii. Wax content of the coated silica

The wax content of the coated silicas is determined by solvent extraction using the Tecator Soxhlet HT2. A known weight of sample is transferred to the "thimble" on the apparatus and extracted with 70 mls of chloroform at reflux for 20 minutes. The thimble is rinsed for 45 minutes, air blown for 5 minutes, removed from the equipment and dried in an air circulated oven at 105°C for 15 mins. The wax content (in % w/w) can be calculated from the weight difference to constant weight.

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SPECIFIC DESCRIPTION OF THE INVENTION

5 The present invention which be further described in the following examples in which examples 1 to 6 describe how to produce an amorphous silica suitable for the present invention whereas example 7 describes a coated silica according to the invention.

Example 1

10 A heated stirred reaction vessel was used for the silicate/acid reaction.

15 Mixing is an important feature in the reaction of silicate and sulphuric acid. Consequently fixed specifications as listed in Chemineer Inc. Chem Eng. April 26th 1976 pages 102-110 have been used to design the baffled heated stirred reaction vessel. Whilst the turbine design is optional to the mixing geometry, a 6-bladed 30° pitched bladed unit has
20 been chosen for the experiments in order to ensure maximum mixing effectiveness with minimum shear.

The solutions used in this Example were as follows:

- 25 i) Sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.29:1 and a SiO_2 content of 17.2% by weight.
- ii) A sulphuric acid solution of specific gravity of 1.12.

30 No electrolyte solution was added.

13.6 litres of water was placed in the vessel together with 0.12 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

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11.4 litres of sodium silicate and 4.8 litres of sulphuric acid were then added simultaneously over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The flow rates of the silicate and acid solutions were uniform throughout the addition period to ensure that a constant pH of 10 was maintained in the vessel.

Silicate slurry was then aged at pH 10 for 50 minutes at 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

Example 2

The same reaction vessel, with the same stirrer, was used as in Example 1.

The solutions used in this Example were as follows:

- i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.29:1 and a SiO₂ content of 16.75% by weight.
- ii) A sulphuric acid solution of specific gravity of 1.13.
- iii) 3.8 litres of a 25% (w/w) sodium chloride solution.

13.6 litres of water was placed in the vessel together with 11.3 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

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4.89 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period. The final pH after the acid addition was 9.

3.8 litres of a 25% (w/w) sodium chloride solution was then added over 18 minutes, the temperature being maintained at 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

Example 3

The same reaction vessel, with the same stirrer, was used as in Example 1.

The solutions used in this Example were as follows:

- i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.29:1 and a SiO₂ content of 17.2% by weight.
- ii) A sulphuric acid solution of specific gravity of 1.12.

13.6 litres of water was placed in the vessel together with 11.5 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

4.84 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution

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was uniform throughout the addition period. The final pH after the acid addition was 11.

5 The slurry was then aged over a period of 20 minutes at a temperature of 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

10 The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

Example 4

15 A larger reaction vessel than the one used in Example 1 but with the same configuration of the vessel geometry, baffles and stirrer was used.

The solutions used in this Example were as follows:

20

i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.28:1 and a SiO₂ content of 16.62% by weight.

ii) A sulphuric acid solution of specific gravity of 1.12.

25

iii) 40 litres of a 25% (w/w) sodium chloride solution.

30

83.5 litres of water was placed in the vessel together with 80.2 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

35

27.96 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period.

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40 litres of a 25% (w/w) sodium chloride solution was then added over 15 minutes, the temperature being maintained at 98°C.

5 Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

The resultant slurry was then filtered and washed with water to remove excess electrolyte, dried and micronised.

10

Example 5

The same reaction vessel, with the same stirrer, was used as in Example 1.

15

The solutions used in this Example were as follows:

i) Sodium silicate solution having a SiO₂:Na₂O ratio of 3.25:1 and a SiO₂ content of 17.1% by weight.

20

ii) A sulphuric acid solution of specific gravity of 1.13.

iii) 4.0 litres of a 25% (w/w) sodium chloride solution.

25 13.35 litres of water was placed in the vessel together with 11.6 litres of sodium silicate solution. This mixture was then stirred and heated to 98°C.

30 5.03 litres of sulphuric acid was then added over a period of 20 minutes with stirring whilst maintaining the temperature at 98°C. The acid flow rate of the acid solution was uniform throughout the addition period.

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4.0 litres of a 25% (w/w) sodium chloride solution was then added over 18 minutes, the temperature being maintained at 98°C.

5 The slurry was then aged during 10 minutes at 98°C.

Sulphuric acid was then added over a period of 10 minutes to give a final slurry pH of 4.

10 The resultant slurry was then filtered and washed with water to remove excess electrolyte dried and micronised.

The physical properties of Examples 1 to 5 are summarised in the following Table 1 wherein:

15

- S.A. = Surface Area to nitrogen (m^2/g)
- P.V. = Total Pore Volume to nitrogen (cm^3/g) (of pores with pore diameter between 1.7 and 300 nm)

20

- P.V.(10-30) = Pore Volume to nitrogen of pores having a diameter between 10 and 30 nm. (cm^3/g)

- $$X = 100 \times \frac{\text{P.V.}(10-30)}{\text{P.V.}}$$

25

- Pore size distribution: D_{10} , D_{50} , D_{90} in nanometers as above defined in "Definitions and Test procedures" section i).

30

- M.E. at 60° = Matting efficiency at 60° at 5% loading (in gloss units) in high viscosity thixotropic system
- M.E. at 85° = Matting efficiency at 85° at 5% loading (in gloss units) in high viscosity thixotropic system

35

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- d_{10} , d_{50} , d_{90} = percentiles of the particle size distribution (microns) after drying and micronization,
- S = Surface Area to CTAB (m^2/g)
- NM means that the parameter was not measured

TABLE 1

Example	1	2	3	4	5
S.A. (m^2/g)	177	209	215	230	NM
P.V. (cm^3/g)	1.09	1.31	0.91	1.78	NM
P.V. (10-30) (cm^3/g)	0.13	0.20	0.16	0.19	NM
X	11.9	15.4	17.6	10.7	NM
S (m^2/g)	55	82	77	74	70
D_{10} (nm)	22	21	16	28	NM
D_{50} (nm)	60	50	50	60	NM
D_{90} (nm)	>100	>100	>100	>100	NM
M.E. at 60°	15	6	6	11	7
M.E. at 85°	36	10	10	26	12
d_{10} (μm)	2.6	3.7	4.0	3.0	4.1
d_{50} (μm)	5.8	7.4	7.6	6.9	7.1
d_{90} (μm)	12.8	14.9	14.3	14.6	20.3

Example 6

A number of preparations have been made, altering the temperature, the percentage SiO₂ of the sol after the first acid addition, the Degree of Neutralization, the NaCl:SiO₂ ratio and the ageing time.

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Preparations are based upon a sol volume of 30 litres, the sol consisting of water, sodium silicate and first acid addition. The method of addition being according to Example 2 or 5 depending on the presence of an ageing step of 10 minutes.

The results are summarised in the following Table 2 wherein.

- $\text{SiO}_2(\%)$ represents the SiO_2 concentration in percent by weight at the end of the first acid addition,
- DofN represents the Degree of Neutralization,
- $\text{NaCl}:\text{SiO}_2$ represents the weight ratio of NaCl and SiO_2 ,
- M.E. at 60° = Matting efficiency at 60° at 3% loading (in gloss units) in high viscosity thixotropic system
- M.E. at 85° = Matting efficiency at 85° at 3% loading (in gloss units) in high viscosity thixotropic system
- d_{10} , d_{50} , d_{90} = percentiles of the particle size distribution (microns) after drying and micronization.
- S = Surface Area to CTAB (m^2/g)
- NM means that the parameter was not measured,

TABLE 2

Sample	1	2	3	4	5
Temperature (°C)	80	80	80	80	88
SiO ₂ (%)	6.6	7.3	7.3	7.3	7.0
10 minutes Ageing	Yes	No	No	Yes	No
DofN (%)	70	70	84	84	84
NaCl:SiO ₂	1:1	1:1	0.5:1	1:1	1:1
d ₁₀ (μm)	4.6	4.5	3.1	3.8	2.7
d ₅₀ (μm)	8.6	9.1	5.9	8.0	4.8
d ₉₀ (μm)	16.5	19.4	12.0	16.9	8.2
M.E. 60°	13	12	20	18	19
M.E. 85°	20	16	45	36	56
S (m ² /g)	150	116	134		

TABLE 2 (CONTINUED)

Sample	6	7	8	9
Temperature (°C)	98	98	98	98
SiO ₂ (%)	6.6	7.0	7.3	7.3
10 minutes Ageing	Yes	No	No	Yes
DofN (%)	84	84	84	70
NaCl:SiO ₂	1:1	0.5:1	1:1	1:1
d ₁₀ (μm)	3.2	3.7	3.2	4.1
d ₅₀ (μm)	6.6	7.4	6.0	9.5
d ₉₀ (μm)	13.7	14.9	10.6	21.0
M.E. 60°	15	14	15	19
M.E. 85°	42	30	38	26

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Example 7

A slurry as obtained under Example 4 was eventually, filtered dried and micronised in order to provide an amorphous silica having the following particle size distribution:

- d_{10} : 4.0 μ m
- d_{50} : 8.6 μ m
- d_{90} : 16.4 μ m

This silica was coated at two levels with microcrystalline wax (Crown Wax) and a ternary wax blend according to EP-A-0,541,359 (Kerawax 2773P).

The Matting Efficiency of the naked silica as well as the coated silica was measured in a low viscosity system. The results are summarized in the following table in which:

- M.E. at 60° = Matting efficiency at 60° at 6.5% loading in low viscosity system (in gloss units)
- M.E. at 85° = Matting efficiency at 85° at 6.5% loading in low viscosity system (in gloss units)

	M.E. 60°	M.E. 85°
Naked silica	53	69
Silica + 3.3 % Crown wax (*)	21	32
Silica + 6.9 % Crown wax (*)	24	38
Silica + 3.3 % Kerawax 2773P (**)	12	15
Silica + 6.9% Kerawax 2773P (**)	12	15

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(*) Crown wax is a microcrystalline wax obtainable from
Petrolite

(**) Commercially available from Kerax - England

5

It is clear that, contrary to the prior art, the coated
silica exhibits matting properties which are better than the
matting properties of the naked silica. In other respects,
the best results in term of matting properties are obtained
using a ternary wax blend as disclosed in EP-A-0,541,359.

10

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CLAIMS

1. Wax coated silica matting agent characterised in that the silica is an amorphous silica having a pore size distribution wherein 90% of the pores have a diameter above 15 nanometers, and less than 20% of the pore volume is in pores having a pore diameter between 10 and 30 nanometers, the wax coating being present in the range from about 2% to about 15% by weight of the matting agent and comprising a hard microcrystalline wax, a plasticising microcrystalline wax, a synthetic polyethylene wax or a mixture thereof.
2. Wax coated silica according to claim 1 wherein the wax coating comprises
 - i. from about 50% to about 90% by weight of a hard microcrystalline wax,
 - ii. from about 5% to about 30% by weight of a plasticising microcrystalline wax, and
 - iii. from about 5% to about 20% by weight of a synthetic polyethylene wax.
3. Wax coated silica according to claim 1 or 2 wherein the amorphous silica has a matting efficiency of below 20 gloss units at an incidence angle of 60° and a loading of 5% by weight in a high viscosity thixotropic system.
4. Wax coated silica according to claim 3 wherein the amorphous silica has a CTAB surface area of less than 100 m²/g.

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5. Process for manufacturing a wax coated amorphous silica according to any of the preceding claims, in which the components of the wax coating are blended by melting, milled to a particle size comparable with the amorphous silica, mixed with the silica in an amount of about 2% to about 15% by weight of the mixture which is then milled in a fluid energy mill to provide a wax coated silica product wherein the amorphous silica is manufactured in a process in which, in a first step, sulphuric acid is added to, or mixed with, a sodium silicate solution having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of between 3.1 and 3.4 to form a slurry, after this first step the degree of neutralisation being between 50% and 88% and the SiO_2 concentration being between 6.5% and 7.5% by weight, the temperature of the slurry being maintained below 100°C and above 85°C , sulphuric acid being afterwards added to reach a pH of about 4, the resulting silica being then washed and dried.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 95/01431

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09C1/30 C09D7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 588 497 (JOSEPH CROSFIELD & SONS) 23 March 1994 see page 3, line 4 - line 7; claims 1-5 ---	1,2,5
Y	EP,A,0 341 383 (DEGUSSA) 15 November 1989 see claims 1,3,6 ---	1,2,5
Y	EP,A,0 541 359 (JOSEPH CROSFIELD & SONS) 12 May 1993 cited in the application see claims 1,4,10 ---	1,2,5
A	US,A,4 097 302 (H. J. COHEN ET AL.) 27 June 1978 ---	
A	GB,A,798 621 (W. R. GRACE & CO.) 23 July 1958 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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 "&" document member of the same patent family

Date of the actual completion of the international search

26 July 1995

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/01431

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